A Study of Combustion and Other Free Radical Processes in the Chemical Shock Tube

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The difficulties which are inherent in the study of certain thermal reactions and in combustion research are well known: difficulty of initiation, the very high rate of reaction once begun, the complexity of the resulting mixture, and in some cases, surface effects. A need for understanding the mechanism of these high temperature reactions still remains a basic problem. The kinetics and energetics of a number of reactions investigated at low temperatures appear to be at least partially understandable. However, considerable deviation from theory is indicated as the reaction temperature is increased.

The outstanding feature that distinguishes high temperature kinetics from low or moderate temperature kinetics is the much larger amount of energy present in the reaction system. As the result of this high energy content, possible deviations from low temperature kinetics may arise. The sources of these deviations are listed as follows:

1. Reaction intermediates that may be somewhat stable at low temperature may decompose rapidly at elevated temperature, supplying chain carriers that may completely change the kinetics of the reaction.
2. Non-equilibrium energy distributions may appear among reactants and products in fast, high temperature reactions.
3. Diatomic and triatomic radicals may be formed in addition to the polyatomic radicals which are usually observed at low temperature.
4. Large numbers of atoms and radicals may be produced which are unknown at lower temperatures.

The conventional kinetic systems are impractical for the study of high temperature reactions since the reactants must be heated rapidly to a high temperature without appreciable reaction occurring before the desired temperature is attained. The single impulse shock tube which has been described by Glick, Squire, and Hertzberg[1] offers a means of considerable flexibility for obtaining more fundamental chemical data. A wide range of reaction temperature is possible, concentrations of reactants can be varied within wide limits and surface effects are eliminated. With the single impulse shock tube, the reaction occurs following the reflected shock wave, and then is quenched by a strong rarefaction. The reaction products can be flushed from the tube and analysed.

Apparatus and Materials

The single-impulse shock tube was made of two-inch stainless steel pipe; three-foot sections were assembled and held in proper alignment by bolted flanges. The general construction is essentially that described by Glick, Squire and Hertzberg.[1] A few minor modifications were required to overcome certain mechanical difficulties.

The arrangement used in these studies was determined by the reaction time desired. A typical arrangement proceeding from one end of the apparatus to the other, is as follows: Expansion tank (twenty gallon capacity; six-foot high pressure driver section; three-foot buffer section (I); three-foot reaction section; six-foot buffer section (II); end plate. Two SLM quartz piezo-electric pressure pick-ups were mounted in buffer section II to measure the velocity of the shock wave by feeding the proper signal to the start and stop of a Berkeley EPUT and Timer model No. 7360. A shock-proof mounting was required for the crystal pressure pick-ups.

The position of the reaction section was chosen after a study of pressure-time traces during the operation of the tube with the pressure pick-up in different positions. These traces were made by using the Kistler Instrument Company piezo calibrator. The output of the calibrator was recorded photographically with a Tektronix Model 535 oscilloscope with No. 53C plug-in dual beam preamplifier unit. The position which was chosen for the reaction section resulted in the reaction occurring in a section which was free from anomalous pressure peaks in the trace.

Two special quick-opening valves were used to isolate the reaction mixture from the buffering gas prior to reaction.

These values were plug type valves in which the plug was bored exactly to the inside diameter of the shock tube. Leakage across the valve and to the atmosphere was eliminated by the use of O-rings in appropriate grooves.

All of the hydrocarbons used with the exception of cyclopropane, were research grade chemicals supplied by Phillips Petroleum Company. The compressed gases were commercially available. The azomethane used was prepared by the oxidation of dimethylhydrazine with mercuric oxide according to the method of Renaud and Leitch.[2]

Experimental Procedure

In preparation for a reaction, all parts of the system were evacuated, flushed with helium, evacuated again, and then filled with helium to the required pressure. The reaction mixture was prepared by introducing helium, and the reactants, into a stainless steel cylinder and mixing by imposing a strong thermal convection. The buffer and reaction sections were all filled to exactly the same pressure, and the quick-opening valve was opened ten-fifteen seconds before the bursting of the main diaphragm.

The reaction products were flushed from the shock tube in a stream of helium through two traps cooled in liquid nitrogen; the second trap was filled with adsorbent charcoal which had been activated by heating to 300°C. in a stream of helium.

The contents of the traps were transferred to gas holders for analysis. Conventional gas chromatographic methods were used; the following analyses were performed with the respective columns:

1. Linde Molecular Seive 5A, 117°: hydrogen, carbon monoxide, and methane.
2. Silica gel 40°: ethane, ethene, and carbon dioxide.
3. Dowtherm A 40°: propane, propene, and all the C_4 hydrocarbons, pentane, and the pentenes.
4. Polyethylene glycol 40°: oxygenated compounds.

A Gow-Mac filament type cell was used with the first three columns; a very sensitive thermistor cell was used in the search for oxygenated compounds.

In almost all of the runs, the composition of the mixture in the reaction section was approximately five mole percent or less.

Other reaction products that could not be separated by gas chromatography were determined by other conventional methods of analysis. The reacted gas was passed into water and formaldehyde was determined as the 2,4-dinitrophenylhydrazone; the acid equivalent, by titration; and peroxides, by titrating with hydrogen iodide according to the procedure of Satterfield, Wilson, LeClair and Reid.[3]

Results

Thermal Decomposition of Azomethane

Azomethane was thermally decomposed at temperatures ranging from 437.5 to 635.2°C. and reaction times of 0.6 to 3.8 milliseconds. At the lower temperatures and at low concentration the dominant reaction leads to the formation of ethane. At higher temperatures and higher initial concentrations, methane, ethylene and propane are formed in large amounts. Linear relationships are obtained when the log azomethane concentration at a particular temperature is plotted against the reaction time. The rate expression for the thermal decomposition of azomethane was determined to be

$$k = 1.24 \times 10^{15} \exp \frac{-46,200}{Rt} \quad \text{sec}^{-1}.$$

Methyl Radical Reaction with Oxygen

Methyl radicals, which were generated by thermally decomposing azomethane, were allowed to react with oxygen at 522°C. and at various oxygen-radical ratios. The results for a 5:1 oxygen-azomethane ratio are given in Table I. The acid formed from the methyl radical-oxygen was determined in only one experiment. From 442×10^{-6} m of azomethane under the above conditions, 26.6 microequivalents of acid was formed. To test the stability of some of the reaction products under the reaction conditions, several reactions between methanol and oxygen and carbon monoxide and oxygen were carried out. For the water-catalysed reaction of CO and oxygen at 632°C. practically all of the CO was recovered unchanged. At 1300°C., however, more than 90 percent of the CO was converted into CO_2.

Table I
Reaction of Methyl Radicals and Oxygen in the Shock Tube at P_{41} = 14.66, T = 522°C.
(Oxygen-Azomethane Ratio = 5:1)

Exp. No.	12-50-(3)	(4)	(5)[b]	(6)	(7)
Reaction Time (milliseconds)	2.6	2.2	0.8	1.5	3.0
Azomethane, μm.					
initial	416	464	440.4	456.4	476
unreacted	14.5	42.8	a	a	a
Products					
C_2H_6	45.6	35.4	a	18.9	72.7
CH_4	96.3	79.0	a	52.4	117.3
CO	197	176	a	138.4	286.4
CO_2	27.6	20.5	a	11.2	82.7
H_2	176	181.6	a	118.2	a
C_2H_4	8.3	9.3	a	6.4	33.2
HCHO	273	a	92.8	378.2	235.0
CH_3OH	a	2.0	a	a	a
Carbon balance	85.8	46.8	10.6	69.1	98.2

[a] Experimental difficulties prevented analysis of these compounds.

b A complete set of analyses for formaldehyde at this temperature shows a maximum in concentration at 2 millisec.

Cyclopropane and n-pentane Reactions

The isomerization of cyclopropane to propylene occurs readily at 760°C. and higher although at long reaction times methane, ethylene, butene and hydrogen are also formed. The methyl radical-induced decomposition of cyclopropane was also studied. At 760°C. the induced reaction leads to heavy carbon deposits on the walls of the shock tube. When the induced reaction was carried out with added oxygen traces of acetaldehyde, formaldehyde and acrolein were detected as the 2,4 DNPH derivatives.

The products formed by the reaction of n-pentane with oxygen are those generally expected of hydrocarbon oxidation at high temperature. A series of experiments were carried out at 877°C.

in which the reaction time was varied from 2.2 to 3.4 milliseconds. The only oxygenated products found were carbon monoxide and carbon dioxide. Oxygenated products with any vestige of the original carbon skeleton are absent even at very short reaction times.

Discussion

The thermal reaction of azomethane in the shock tube appears to proceed by a unimolecular process when the initial azomethane concentration is reasonably low, the reaction time is short and the reaction temperature is not too high. The formation of propane in the reaction system at the higher temperatures and at long reaction times suggest that ethyl radicals are present in great abundance. Products involving methyl addition to azomethane to form tetramethylhydrazine were not detected in any of the experiments which indicates that this reaction is not important at these high temperatures.

The Arrhenius activation energy of 46,200 cal for the thermal reaction is in reasonably good agreement with the literature values.

The reaction of methyl radicals and oxygen at high temperatures is extremely complicated. There is an increase in the rate of decomposition of azomethane in the presence of oxygen somewhat over that of the pure thermal reaction. Although the results are not quantitative nor complete, this evidence suggests that chain reactions involving methyl radicals, oxygen or reactive intermediates become important at these high temperatures.

Previous investigators have explained the major products of the reaction of methyl radicals and oxygen by these reactions

$CH_3 + O_2$	$\longrightarrow$	CH_3OO	I
$CH_3 + O_2$	$\longrightarrow$	$HCHO + OH$	II
CH_3OO	$\longrightarrow$	$HCHO + OH$	(1)
$HCHO$	$\longrightarrow$	$H_2 + CO$	(2)
$CH_3 + HCHO$	$\longrightarrow$	$CH_4 + CHO$	(3)
$CHO + OH$	$\longrightarrow$	$HCOOH$	(4)
$2\ CH_3OO$	$\longrightarrow$	$2\ CH_3O + O_2$	(5a)
$2\ CH_3O$	$\longrightarrow$	$CH_3OH + HCHO$	(5b)
$CH_3O + RH$	$\longrightarrow$	$CH_3OH + R$	(5c)
$CHO + O_2$	$\longrightarrow$	$CO_2 + OH$	(6)

A number of reaction paths are available to account for the products found in low yield in this reaction and are of minor importance.

Considerable uncertainity still exists as to the nature of the initial reaction of methyl radicals and oxygen. At temperatures from 0°C. to at least 200°C., reaction I is attractive since the subsequent reactions (eq. 5a, 5b) can adequately explain methanol formation. Reaction II leads to no plausible mechanism by which methanol is formed. Only traces of methanol were formed in the oxidation reactions at 503°C. Methanol is relatively stable at this temperature, but only traces of methanol were found. Reactions 5b and 5c do not appear important at this temperature.

Methoxy radicals, formed from dimethylperoxide and thermally decomposed yield formaldehyde and methanol as major products. When oxygen is present, only traces of methanol are detected and CO_2 becomes the major product.

A comparison of the CO_2 analyses from methyl and methoxy radical experiment supplies evidence that the total amount of methyl radicals that go through a methoxy intermediate is probably a good deal less than 5 percent.

The large amount of formaldehyde formed in all stages of the reaction reflects its importance as an intermediate in the oxidation mechanism. The reaction of methyl radicals and formaldehyde, and possibly the formyl radical, partially explain the high methane concentration. When the easily abstractable hydrogen of formaldehyde become readily available, especially at the later stages of the reaction, methane becomes a major product.

Reaction involving peroxide, hydrogen peroxide or hydroperoxide formation apparently do not take place to any appreciable extent at these temperatures.

The conversion of CO to CO_2 at 632°C. is a very slow reaction and although a small amount of CO_2 may be formed from CO, other reactions leading to CO_2 are much more likely to occur.

Although many of the radicals described have been identified in combination reactions by mass spectrometry the importance of many of these species in a chain mechanism at high temperature still cannot be confirmed.

Pentane was chosen for this study since it is intermediate between the simple hydrocarbons and higher molecular weight

hydrocarbons which are important liquid fuels. Pentane, a relatively simple hydrocarbon undergoes reactions that are difficult to interpret. Oxygenated organic products, aldehyde, keton, or acids are absent in the products. Evidently, once a pentane molecule becomes a radical in the presence of oxygen at high temperature it rapidly undergoes complete degradation to carbon monoxide and carbon dioxide. A certain amount of radical decomposition leads to olefin plus a lower alkyl radical. The rather uniform rate of oxidation of pentane over a wide range of oxygen concentration suggests that the radical chains are long.

Certain high temperature combustion studies can be carried out successfully in the chemical shock tube. The oxidation reaction can be carried only to the desired stage and stopped.

While the experimental results do not permit a reaction mechanism to be proposed, an insight of the high temperature problem, with all of its complexities, has been obtained.

References

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